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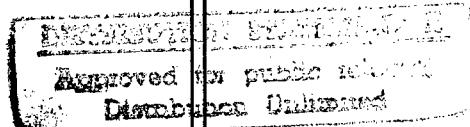
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UNITED STATES ATOMIC ENERGY COMMISSION

THE POWDER METALLURGY OF ZIRCONIUM—
TIN ALLOYS (PART I)

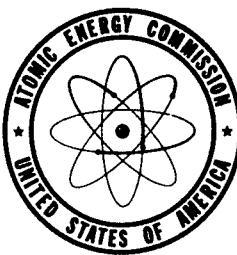
By

Henry H. Hausner
Richard M. Treco



February 1, 1952

Sylvania Electric Products, Inc.
Bayside, New York



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THE POWDER METALLURGY OF ZIRCONIUM-TIN ALLOYS (PART I)

By
Henry H. Hausner
Richard M. Treco

ABSTRACT

An exploratory investigation was made of the feasibility of manufacturing zirconium-tin alloys by powder metallurgical methods. Several series of zirconium-rich alloys were prepared from commercial grade tin powder and (1) ZrH₂ powder made from Grade III crystal bar, (2) ZrH₂ powder made from Grade I crystal bar, or (3) ZrH₂ powder made from Grade C Bureau of Mines zirconium sponge.

The corrosion rates and other physical properties of the various alloys are given and the results from crystal bar zirconium were compared with those from zirconium sponge.

A brief study was also made of resistance-sintering of zirconium-tin alloys made from zirconium-sponge hydride powder and tin powder.

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I. INTRODUCTION

It is known that zirconium corrodes in water at 600°F and that the corrosion rate depends largely on the type and amount of impurities in the zirconium. Some time ago it was found at several AEC installations that small amounts of tin added to the zirconium, by melting and forming a zirconium-tin alloy, practically inhibits the corrosion.

This report describes the preliminary investigations for manufacturing zirconium-tin alloys by powder metallurgical methods; it shows the results obtained from these preliminary tests and the advantages of making zirconium-tin alloys from metallic powders and hydrides.

II. RAW MATERIALS

The alloys described in this report were made from zirconium crystal bar, Grades I and III, and from Bureau of Mines (BM) zirconium sponge, Grade C. Commercial tin powder was used for the tin additions, the spectrographic analysis and particle size distribution of which are listed in Tables I and II.

The zirconium component in these alloys was made from zirconium hydride powder prepared by hydriding the crystal bar or the sponge in purified hydrogen at 800°C and as described in report NYO-1127*. The zirconium hydride powder was screened through a 325-mesh sieve, resulting in an average particle size of 5 and 7 microns. The mean particle size of the tin powder was 5.7 microns.

III. EXPERIMENTAL PROCEDURE AND RESULTS

A. Alloys Made from Grade III Crystal Bar

The first series of alloys consisted of three compositions containing 0.3, 5.2 and 14.3 w/o tin. The zirconium hydride powder for these alloys was made from Grade III crystal bar, and as-received tin powder of the commercial grade, described above, was used. The powders were mixed for 1-1/2 hours in argon atmosphere and then compacted at 50 tsi in a steel die. The compacts, approximately 3" x 1/4" x 1/4", were sintered in a graphite sintering boat in vacuum at 1150°C for three hours in order to decompose the hydride.

* R. P. Angier and H. H. Hausner, "An Investigation into the Powder Metallurgy Processing of Zirconium Dihydride and Zirconium Powders Prepared from Zirconium Crystal Bar", April 10, 1950 (NYO-1127).

TABLE I

PARTICLE SIZE DISTRIBUTION OF COMMERCIAL- GRADE TIN POWDER	
Particle Size Range, Microns	w/o
149	0.13
74-149	0.54
44-74	2.42
30-44	3.8
20-30	11.8
16-20	11.2
14-16	4.1
12-14	6.7
10-12	8.1
8-10	8.6
6-8	9.4
5-6	3.0
4-5	5.2
3-4	8.1
2-3	11.8
0-2	4.9

Average Particle Size
(Fisher Sub-Sieve Size) = 5.7 microns

TABLE II

SPECTROGRAPHIC ANALYSIS OF COMMERCIAL GRADE TIN POWDER	
Element Detected	w/o
Bi	0.1-1.0
Pb	"
Fe	0.01-0.1
Sb	"
Si	"
Ag	0.001-0.01
As	"
Ca	"
Cu	"

Alloys Made from Grade III Crystal Bar (Cont'd)

The sintered alloys obtained by this method may be best characterized as follows: all specimens were of extremely low density, and close examination of the sintered bars after surface grinding showed the presence of holes, probably caused by localized tin segregation resulting from the presence of coarse tin particles. On account of their extreme porosity, these specimens were not expected to be corrosion resistant. The results of the corrosion test in 600°F water are listed in Table III.

TABLE III

CORROSION RATE (160 hr IN 600°F WATER)
OF LOW-DENSITY Zr-Sn ALLOYS MADE
BY SINTERING AT 1150°C

Sample No.	W/o Sn	Density, gm/cc	Corrosion Rate, mg/cm ² /mo
40-1A	0.3 "	6.32	102.1
40-1B	0.3	6.32	221.5
40-2A	5.2	6.28	0.95
40-2B	5.2	--	0.80
40-3A	14.3	6.1	263.0
40-3B	14.3	6.2	282.0

(Crystal Bar Zirconium)

Although the corrosion rate of the 0.3 and 14.3 w/o tin specimens was extremely high, the corrosion rate of the 5.2 w/o tin samples was fairly low and was less than 0.5% of that of the two other alloys. These results, although not satisfactory, were very encouraging and showed that an addition of approximately 5% tin, even when made by powder metallurgical methods under the most unfavorable circumstances (Grade III crystal bar, coarse tin powder particles, and low sintering temperature), effectively prevented excessive corrosion of this material.

B. Alloys Made from Grade I Crystal Bar

The next series consisted of alloys containing 0, 1, 3, 5, 7 and 10% tin which were made under considerably more favorable conditions than those of the first series. The zirconium hydride powder for these alloys was made from Grade I crystal bar. The coarse tin particles which caused the porosity in the first series were eliminated by screening the tin powder through a 325-mesh screen. The two powder components were mixed in argon atmosphere for two hours, the mixtures compacted at 50 tsi, and the compacts sintered at 1270°C for ten hours in vacuum. Table IV shows the results of this test; it contains the densities of the compacted and sintered samples, the linear and volume shrinkages, the weight loss of the specimens during sintering as well as average grain size, hardness, electrical resistivity and corrosion rate of these alloys when tested at 190°C in water at 600°F. The following analysis of the data shown in Table IV offers valuable information concerning the possible production of zirconium-tin alloys by powder metallurgical methods.

1. Density

The sintered densities of the samples of this series were considerably higher than those of the series described in Table III. This was due to better raw materials and more favorable mixing and sintering conditions. The alloys showed slightly lower densities than the corresponding alloys made by melting, although no microscopic porosity was observed. The 5% tin alloy made by melting has a density of 6.65 gm/cc whereas the same alloy made in the above described method of sintering has a density of 6.58 gm/cc as shown in Fig. 1. These lower densities are due to the fact that the optimum mixing, compacting and sintering conditions have not, as yet, been established. There are, however, reasons to believe that the ideal densities of these alloys can also be obtained by powder metallurgical methods.

2. Shrinkage During Sintering

Table IV shows that the volume shrinkage of the alloys decreases slightly with increasing amounts of tin, showing that the ratio of pressed density to sintered density increases slightly with increasing tin content. The differences

TABLE IV
PROPERTIES OF Zr-Sn ALLOYS MADE BY SINTERING AT 1270°C
(CRYSTAL BAR ZIRCONIUM)

Sample No.	Tin Content w/o	(1) Density as Compacted, gm/cc			(2) Shrinkage During Sintering			Wt. Loss %	Density as Sintered, gm/cc	Av. Grain Diam., mm	Hardness RA	Electrical Resistivity micromhm-cm	(4) Corrosion Rate, mg/cm ² /mo
		Length %	Width %	Height %	Volume %								
56-1	0	4.89	10.0	10.1	5.8	23.8	2.05	6.46	0.082	62	53.8	17.9	
56-2	1	4.89	10.2	10.1	6.0	24.1	2.02	6.49	0.067	63	109.1	3.11	
56-3	3	5.05	8.5	9.4	6.3	22.3	1.98	6.51	0.088	65	105.2	0.72	
56-4	5	5.07	8.6	9.1	6.6	22.4	1.92	6.58	0.079	65	123.3	0.16	
56-5	7	5.10	8.2	9.0	6.9	22.3	1.84	6.61	0.093	66	144.4	0.51	
56-6	10	5.19	7.8	8.6	7.5	22.0	1.85	6.65	0.068	66	161.2	0.49	

- (1) Compacted at 50 tsi
- (2) Sintering time 10 hr
- (3) Determined microscopically
- (4) Corrosion test in 600°F water for 160 hr

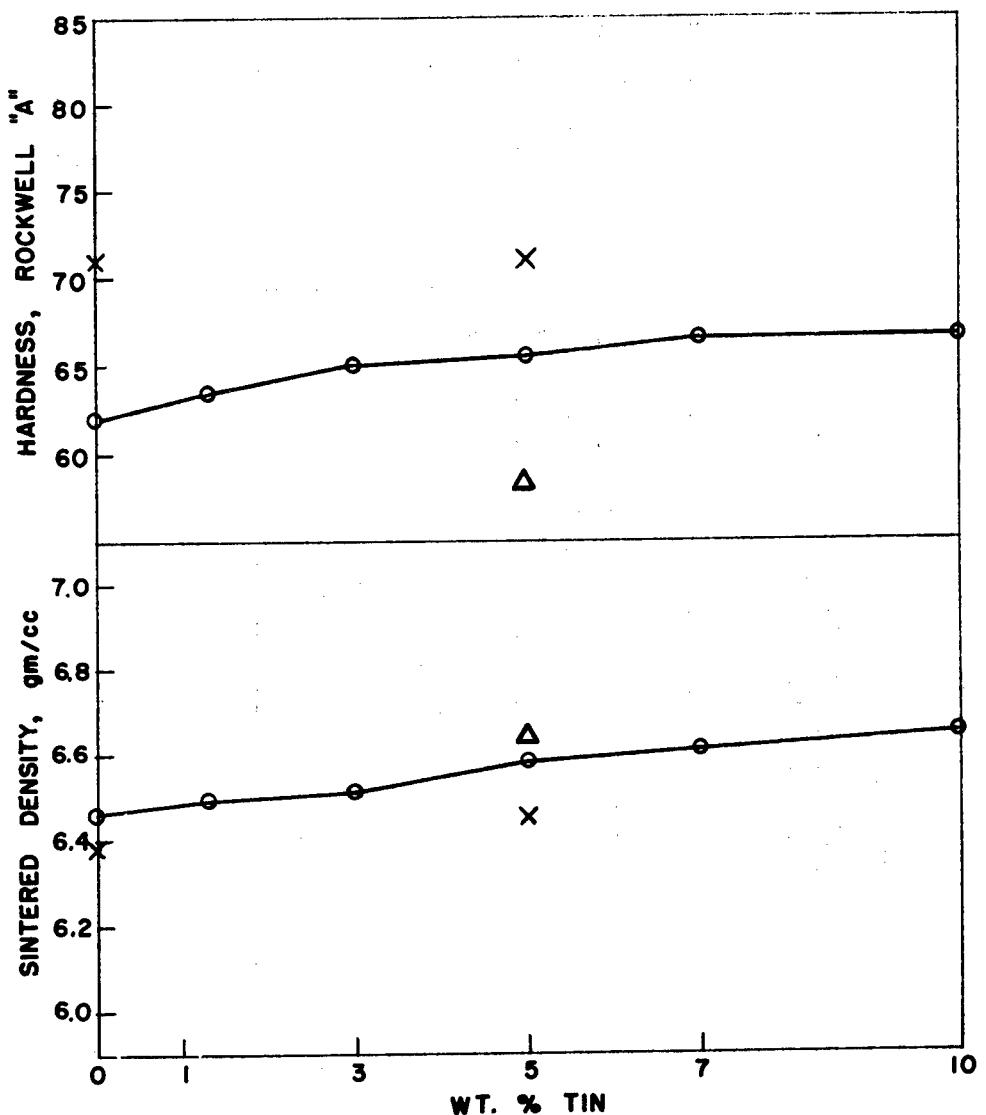


Fig. 1 Properties of Zr-Sn alloys sintered 10 hr at 1270°C.

O = Alloy made from crystal bar Grade I ZrH₂ powder.
X = Alloy made from BM sponge Grade C ZrH₂ powder.
Δ = Alloy made by arc melting BM sponge (Comparison).

Shrinkage During Sintering (Cont'd)

in linear shrinkage in the direction of the compacting pressure perpendicular to these directions are remarkable, and even permit some conclusions to be drawn on the compressibility of the mixed powders. The linear shrinkage data are plotted in Fig. 2 and show a decreasing shrinkage in length and width (axes perpendicular to the compacting direction) with increasing tin content, but an increasing shrinkage in height (in the direction of compacting). The increasing shrinkage in the one direction and the decreasing shrinkage in the other direction explains the relatively small differences in volume shrinkage although the linear shrinkages are considerable. This also shows that the compressibility of the mixture decreases with increasing tin content, indicating that mixtures containing a greater percentage of tin are to be compacted at higher pressures. The presence of an intermetallic zirconium-tin compound may also effect the shrinkage if this compound has a greater specific volume.

3. Weight Loss During Sintering

The weight losses during sintering of these specimens, as listed in Table IV, correspond precisely to the loss of hydrogen during the decomposition of the zirconium hydride. Thus, with decreasing amount of zirconium, the weight loss decreases. No loss of tin by evaporation during vacuum sintering could be observed at temperatures up to 1270°C.

4. Hardness

The hardness of the alloys increases slightly with increasing amount of tin, from $R_A = 62$ for sintered zirconium with no addition up to $R_A = 66$ for the 7 and 10% alloys. The same alloys made by arc melting show a slightly lower hardness, as shown in Fig. 1.

5. Electrical Resistivity

The resistivity data of the alloys listed in Table IV are plotted in Fig. 3 and show a general increase with increasing amount of tin in the compound. There is, however, a definite break in the curve for the 1% tin alloy which may have some connection with the solubility limit of tin in zirconium, although this would place the upper limit of solubility between 1 and 3% rather than the generally accepted 5% tin value. A comparison between the 5% alloy made by powder metallurgy and arc-melting methods, respectively, show that the sintered alloy has a resistivity of 123.3 microhm-cm, whereas the arc-melted material has a resistivity of 116.4 microhm-cm.

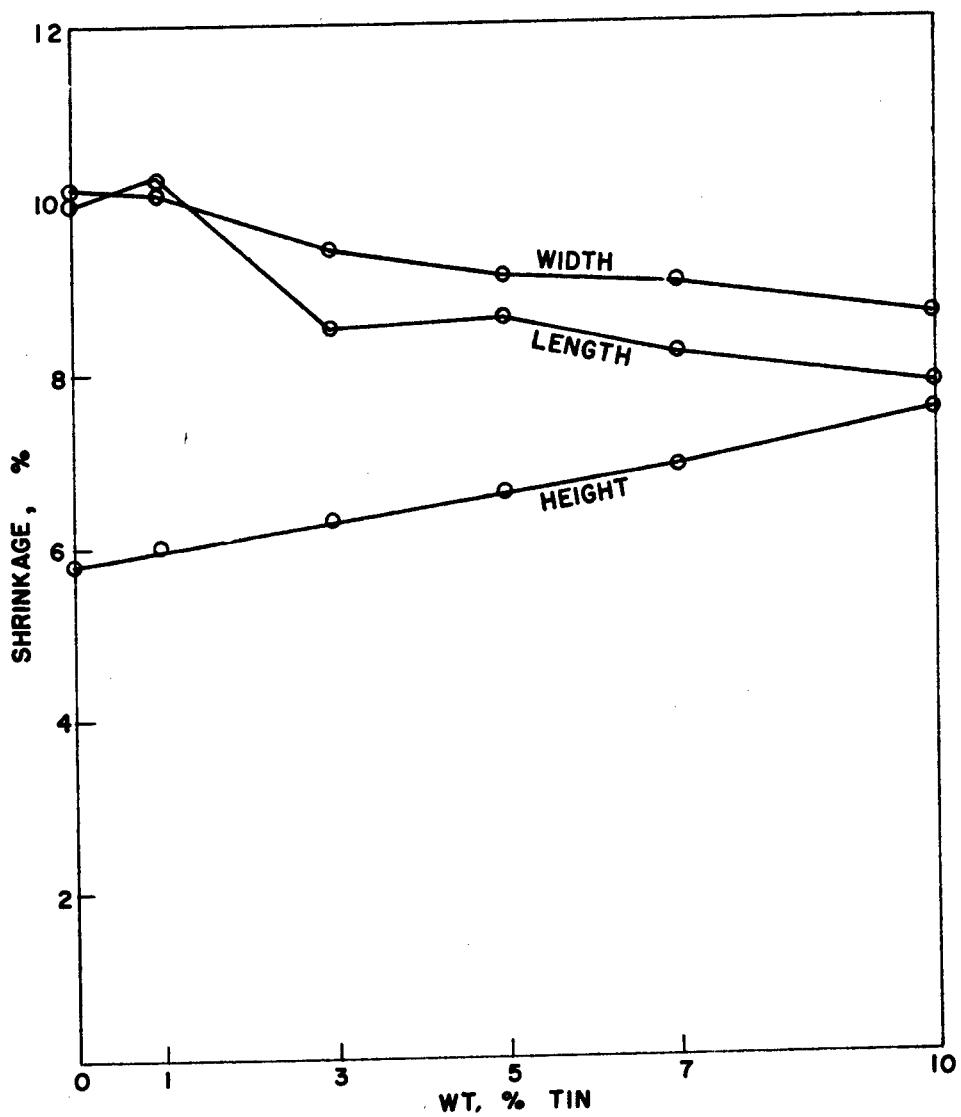


Fig. 2 Linear shrinkage of Zr-Sn alloys during sintering
for 10 hr at 1270°C.

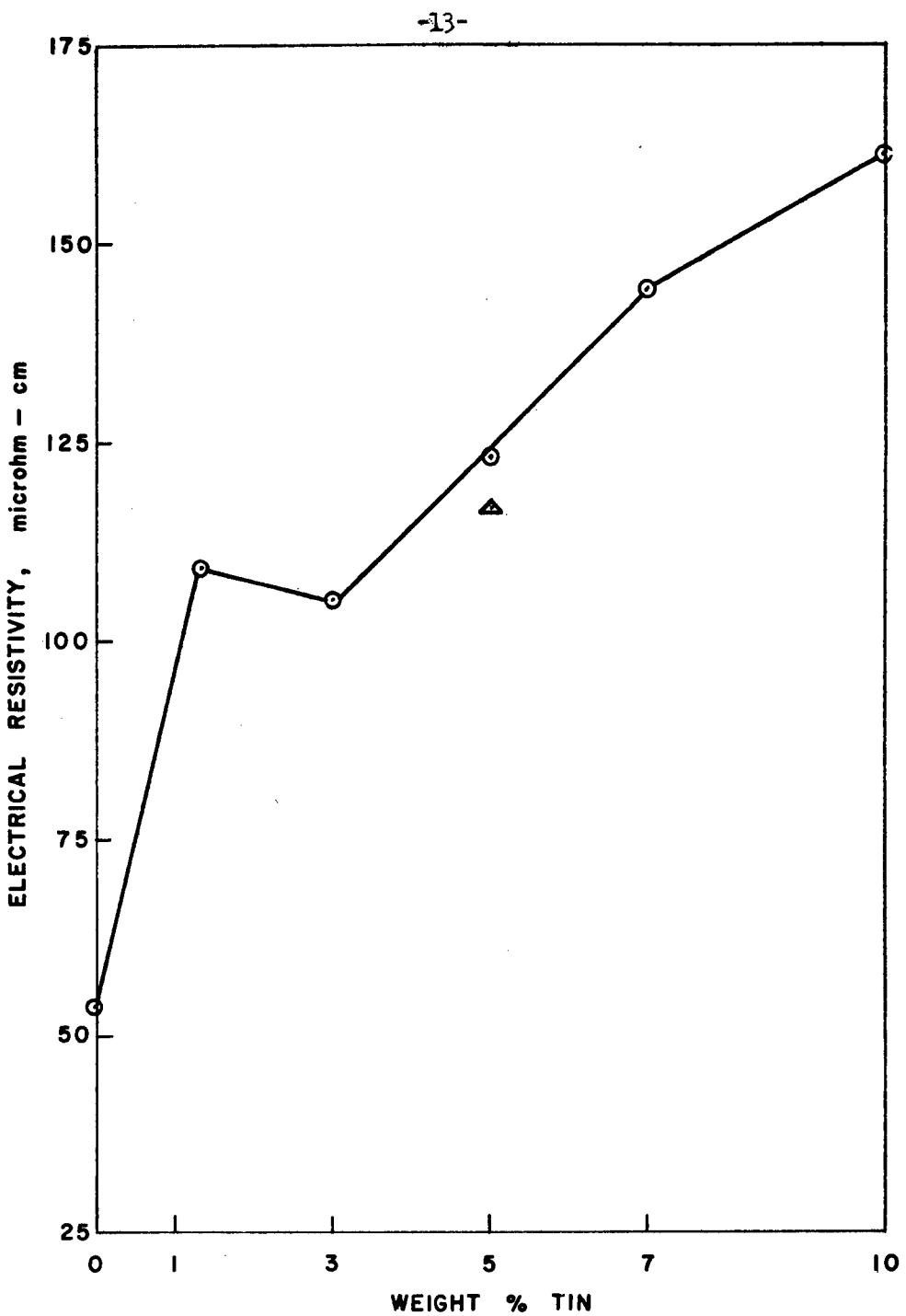


Fig. 3 Electrical resistivity of Zr-Sn alloys (room temperature).

O = Alloy made from crystal bar Grade I ZrH_2 powder.
Δ = Alloy made by arc melting BM sponge (Comparison).

6. Microstructure and Grain Size

Figs. 4, 5 and 6 show the structures and distribution of the tin compound for the 0, 5 and 10% alloys. The average grain size varies between 70 and 90 microns, and no correlation between grain size and tin content could be observed. The grain size data for all the alloys fell within a narrow range equivalent to a single grain size bracket of the ASTM standards for non-ferrous metals.

7. Corrosion

When tested in 600°F water for 160 hr. the corrosion rate of the sintered zirconium without any tin additions was very high, as shown in Fig. 7. This may be explained by the relatively low density of the specimen, as discussed above. Although the densities of all specimens were on the low side, the corrosion rate decreased considerably by addition of tin and showed a minimum of 0.16 mg/cm²/mo for the 5% tin alloy. This is only 1% of the corrosion rate of the sintered crystal bar ZrH₂, without the tin addition and made under identical fabricating conditions.

8. Recrystallization and Grain Growth

The recrystallization process has been studied metallographically in sintered alloys containing 1, 3, and 5% tin. These results will be described in detail in report #SEP-87.

C. Alloys Made From Grade C Sponge

A third series of tests was made by using Bureau of Mines Grade C zirconium sponge as a raw material for the hydride powder. The sponge was used without previous purification and hydrided in precisely the same way as the crystal bars for the series described under Sections A and B. The tin powder was the same as for the series described under Section B. A 5% tin alloy was made by using the hydrided BM sponge, and the two component powders were mixed, compacted and sintered in the same was as described under Section B (50 tsi, 1270°C for 10 hr in vacuum). A sintered zirconium bar made from hydride sponge without any tin additions was made in a similar way for purposes of comparison. The results of these tests are shown in Table V. Both specimens made from the Bureau of Mines sponge are characterized by the low compacted and sintered densities, by the higher rates of shrinkage during sintering and mainly by the weight loss during sintering of approximately 5%, as compared with the 2% weight loss when crystal bar material was used. This weight loss of more than twice that of the specimens made from



Fig. 4 Sintered zirconium made from hydrided zirconium crystal bar powder, compacted at 50 tsi and sintered at 1270°C for 10 hr in vacuum.

Sample #56-1 Polarized light, 200X

Fig. 5 Sintered Zr-Sn alloy made from hydrided zirconium crystal bar powder + 5% tin powder, compacted at 1270°C for 10 hr in vacuum.

Sample #56-4 Polarized light, 200X

Fig. 6 Sintered Zr-Sn alloy made from hydrided zirconium crystal bar powder + 10% tin powder, compacted at 50 tsi and sintered at 1270°C for 10 hr in vacuum.

Sample #56-6 Polarized light, 200X

TABLE V
PROPERTIES OF Zr-Sn ALLOYS MADE BY SINTERING AT 1270°C
(BM SPONGE ZIRCONIUM)

Sample No.	Tin Content w/o	(1) Density as Compacted gm/cc			(2) Shrinkage During Sintering			Wt. Loss %	Av. Grain Diam. mm	Hardness RA	Electrical Resistivity microm-cm	Corrosion Rate mg/cm ² /mo
		Length %	Width %	Height %	Volume %							
56-7	0	4.48	14.3	14.3	6.0	30.9	5.07	6.38	-	71	-	High
56-8	5	4.64	12.8	13.0	8.8	30.8	4.91	6.45	-	71	-	2.16

- (1) Compacted at 50 tsi
(2) Sintering time 10 hr
(3) Determined microscopically
(4) Corrosion test in 600°F water for 160 hr

Alloys Made From Grade C Sponge (Cont'd)

crystal bar zirconium hydride can be explained by the loss of volatile magnesium and magnesium chloride existing in the BM zirconium sponge. The presence of these large amounts of impurities explains the low densities obtained, the high rate of shrinkage, and especially the high rate of corrosion as shown in Table V. The microstructure of the sintered sponge hydride (Figs. 8a and 8b) shows the high porosity of this material.

The substitution of BM zirconium sponge for crystal bar produced another undesirable effect in that a reaction of the compact with the graphite sintering boat was accelerated to such an extent that these compacts stuck to the boat so badly that shrinkage was hindered and cracks formed.

These tests have shown that BM zirconium sponge has to be purified carefully before being used for powder metallurgical purposes and a method for purification is now being studied.

D. Resistance Sintering

An entirely different approach in the sintering of zirconium-tin powder mixtures was tried by application of resistance-sintering methods such as is practised in the manufacturing of sintered tungsten. To this end, a bar of approximately 6" x 3/8" x 3/8" was made by mixing hydride powder produced from BM zirconium sponge and 5% tin powder of -325 mesh size and by compacting the mixture at 75 tsi. The compact was presintered for 25 minutes at 850°C in a vacuum furnace to decompose the hydride and strengthen the green compact. During the presintering operation the bar did not react with the graphite boat. The bar considerably increased in strength, although no apparent densification took place during presintering. The presintered bar was placed in the water-cooled grips of a vacuum sintering bottle, such as used for sintering tungsten, with one of the grips floating on mercury to allow free shrinkage. The bottle was evacuated to 0.25 μ , after which the bar was heated by alternating current for one hour at 1400°C. Power required for this heating was 24 kw at 3.3 amp. After 1 hour at 1400°C, density had increased to 5.98 gm/cc. Since densification was incomplete, the resistance sintering was repeated for 1 hour at 1500°C, after which the bar appeared to be fairly well sintered, having a density of 6.54 gm/cc and a hardness of $R_A = 65$.

The rapid cooling through the alpha-beta transformation, induced by the water-cooled grips, resulted in finer, irregularly shaped grains with no evidence of the zirconium-tin compound at 100X. Examination at higher magnification, however, shows that the compound precipitation was not suppressed, but occurred as very fine, well-dispersed spheroids, as shown in Fig. 9.

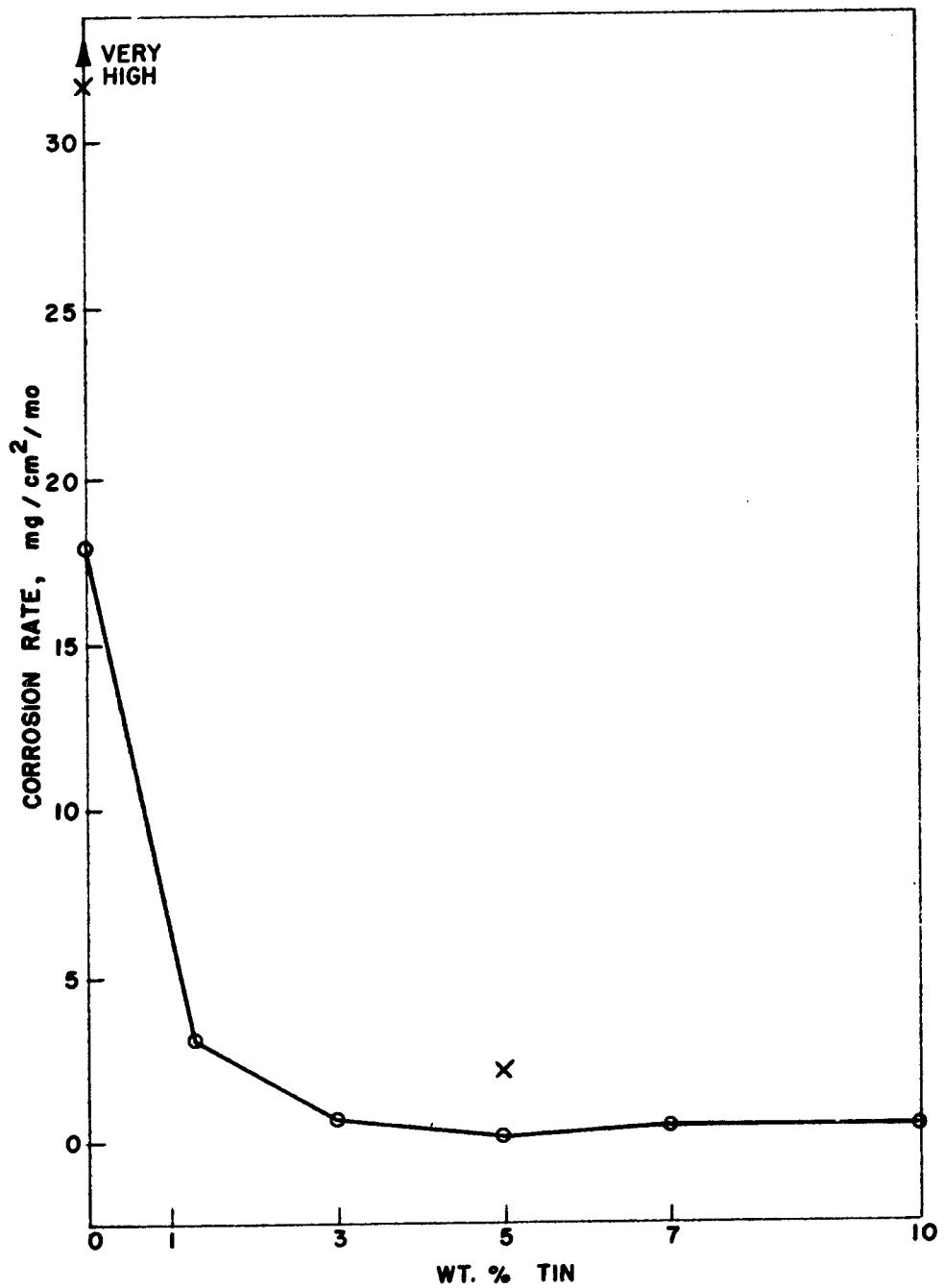
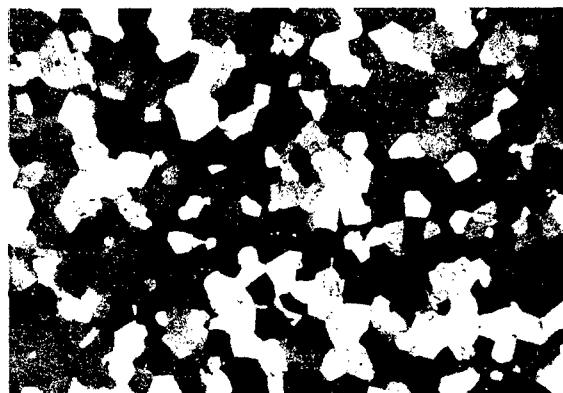


Fig. 7 Corrosion rate of Zr-Sn alloys after 190 hr in 600°F water; sintered 10 hr at 1270°C.

○ = Alloy made from crystal bar Grade I ZrH₂ powder.
△ = Alloy made from BM sponge Grade C ZrH₂ powder.



(a) Sample #56-7. Bright field, 200X



(b) Sample #56-7. Polarized light, 200X.

Fig. 8 Sintered zirconium made from unpurified hydrided zirconium sponge powder, compacted at 50 tsi and sintered at 1270°C for 10 hr in vacuum.

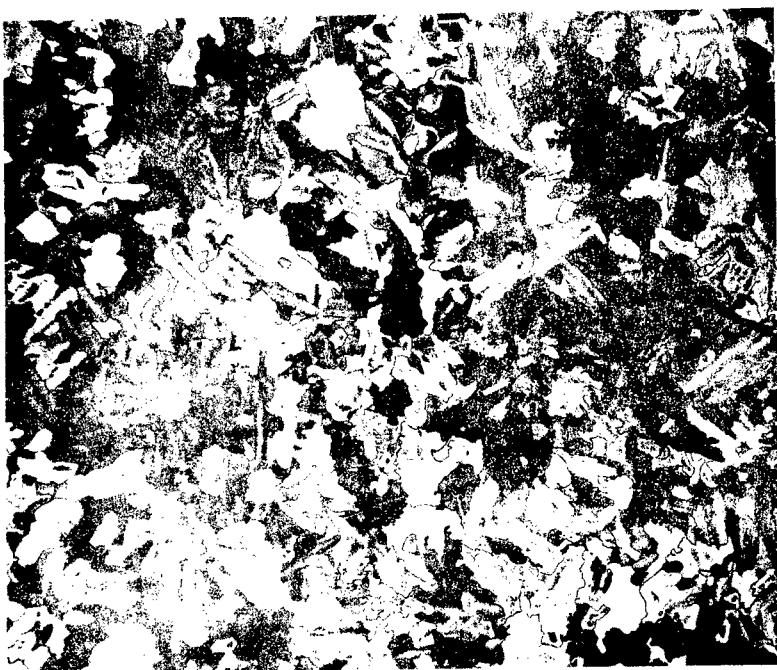


Fig. 9 Resistance-sintered Zr-Sn alloy, made from unpurified hydrided zirconium crystal bar powder + 5% tin powder, compacted at 70 tsi and presintered in vacuum at 850°C for 25 min and resistance sintered in vacuum at 1500°C for 1 hour.

Sample #T-3

Polarized light,
200X

IV. CONCLUSION

Zirconium-tin alloys can be made successfully by powder metallurgy methods. No difficulties in this process are encountered when the zirconium component of these alloys is prepared from crystal bar. When BM zirconium sponge is used for this method, magnesium and magnesium chloride impurities must be removed before the sponge is used. A partial purification of the powder prepared from sponge can be obtained during the sintering treatment. This purification, however, is not a complete one and results in an excessive shrinkage, which is very difficult to control. A new method for purification of the sponge in combination with the hydriding process is under investigation.